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(54) Fixation of reactive dyeings and  
optical brightenings on polyamide  
blends

(57) Dyeings on mixed textile  
substrates of cotton and natural or  
synthetic polyamides, in which the  
cotton component is dyed with direct  
or reactive dyes and the polyamide  
with acid or reactive dyes, are fixed by

aftertreatment with a reaction product  
of an amine with cyanamide, DCDA,  
guanidine or biguanide or with a  
precondensate of the above with an  
N-methylol compound and a catalyst.  
The N-methylol compound is an N-  
methylol derivative or urea, melamine,  
guanamine, triazinone, urone,  
carbamate or acid amide. Where a  
precondensate and catalyst are used a  
heat curing step is required.

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## SPECIFICATION

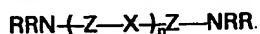
## Improvement in or relating to organic compounds

- This invention relates to a process for
- 5 improving the fastness properties of dyes and optical brighteners on mixed textile substrates.
- The invention provides a process for improving the fastness properties of dyestuffs or optical brighteners on a substrate comprising a mixture of
- 10 natural or synthetic polyamide fibres and hydroxy group-containing fibres, by applying to the dyed, printed or brightened substrate either
- A) a polybasic compound which is the product of reacting a mono- or polyfunctional primary or
- 15 secondary amine with cyanamide, dicyandiamide (DCDA), guanidine or biguanidine; whereby up to 50 mole % of the cyanamide, DCDA, guanidine or biguanidine may be replaced with a dicarboxylic acid or a mono- or di-ester thereof, said product A)
- 20 containing reactive hydrogen atoms bound to nitrogen, or
- B) a precondensate formed by reacting A) above with
- C) an N-methylol derivative of a urea,
- 25 melamine, guanamine, triazinone, urone, carbamate or acid amide applied to the substrate together with
- D) a catalyst for the crosslinking of N-methylol compounds of the type C) above.
- 30 When the precondensate B) and catalyst D) are applied, then a final heat-curing step is carried out.
- Component A) is preferably the reaction product of a monofunctional amine of formula Ia



Ia

- 35 or a polyfunctional amine of formula Ib



Ib 100

- in which each R independently is hydrogen or a  $\text{C}_{1-10}$  alkyl group unsubstituted or monosubstituted with hydroxy,  $\text{C}_{1-4}$  alkoxy or
- 40 cyano, provided that in formula Ia, at least one R is other than hydrogen;
- n is a number from 0 to 100;
- Z, or each Z independently when  $n > 0$ , is  $\text{C}_{1-4}$  alkylene or hydroxyalkylene; and
- 45 X, or each X independently when  $n > 1$ , is  $-\text{O}-$ ,  $-\text{S}-$  or  $-\text{NR}-$  where R is as defined above, provided that the amine of formula Ib contains at least one reactive  $-\text{NH}-$  or  $-\text{NH}_2$  group,
- 50 with a cyanamide, dicyandiamide (DCDA) or guanidine.
- More preferably, component A) is the reaction product of a polyfunctional amine of formula Ib with cyanamide, DCDA or guanidine. In the amines
- 55 of formula Ib, R is preferably hydrogen or  $\text{C}_{1-4}$  alkyl or hydroxyalkyl, more preferably each R is hydrogen. n is preferably a number from 0 to 30, which may be non-integral representing an average value. More preferably n is an integer
- 60 from 1 to 6. Z is preferably a 1,2-ethylene, 1,3-

propylene or 1,3-(2-hydroxypropylene) group, X is preferably  $-\text{NR}-$ , most preferably  $-\text{NH}-$ .

- Particularly preferred amines are diethylene triamine, triethylene tetramine and higher
- 65 polyethylene polyamines, polypropylene polyamines, or poly(hydroxypropylene) polyamines containing up to 8, preferably to 6, N atoms.

- In the reaction with cyanamide, DCDA, guanidine, or biguanidine, the amines may be in the free base or in salt form, for example in the carbonate form, and mixtures of amines may be used. Preferred reagents are guanidine and DCDA, particularly DCDA and particularly preferred
- 70 components A) are the reaction products of diethylene triamine, triethylenetetramine or
- 75 3-(2-aminoethyl)-aminopropylamine with DCDA.

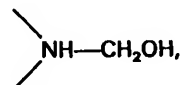
- Components A) are known, and their preparation is described for example in British Patent 657 753 and in US Patent 2 649 354.
- 80 Suitably the reagents are reacted together in the absence of water at elevated temperatures, optionally in the presence of a non-aqueous solvent. Preferably the reaction is carried out in the absence of solvent at a temperature of
- 85  $140-160^\circ\text{C}$ , and with evolution of ammonia. The reagents are preferably reacted in a molar ratio of 0.1 to 1 mole of cyanamide, DCDA, guanidine or biguanidine per mole of reactive  $-\text{NH}$  or  $-\text{NH}_2$  groups, and when DCDA is reacted
- 90 with a polyalkylene polyamine, the molar ratio of the reactants is more preferably from 2:1 to 1:2, particularly about 1:1.

- The products A) are near-colourless viscous liquids or solids which are basic in character,
- 95 water-soluble either in the free base or salt form, and contain reactive hydrogen atoms bonded to nitrogen. The products are preferably miscible with water in all proportions.

- Before being reacted with N-methylol compound C) it is preferred that product A) be neutralised to a pH value of 7-8, e.g. by addition of inorganic or organic acids, preferably hydrochloric or sulphuric acids, to an aqueous solution of A). It may be desirable after
- 105 neutralisation with acid to concentrate the neutralised solution of A) before addition to C); for example the product A) may be converted to a powder by spray drying.

- The components C) are generally those water-soluble N-methylol compounds which are known as crosslinking agents for cellulose fibres, and are used to impart a crease-resistant finish to cellulose fabrics. The compounds may contain free N-methylol groups

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- or these may be etherified. Preferred ether derivatives are the lower alkyl ethers having 1 to 4 carbon atoms in the alkyl groups. Examples of suitable N-methylol compounds are given in
- 120 British Patent Application 2 070 006 A.

Particularly suitable are hydrolysis-resistant

reactive resin precursors, for example N,N'-dimethylol-4,5-dihydroxy- or 4,5-dimethoxy-ethyleneurea, N,N'-dimethylol-4-methoxy-5,5-dimethyl-propyleneurea and N,N'-dimethyl carbamates, optionally in etherified form. Preferred ether forms are the methyl and ethyl derivatives.

The N-methylol compound C) is generally obtained in the form of an aqueous solution containing approx. 40—50% by weight of C), and may be used as such in the reaction with A), or may be further diluted with water.

The reaction being components A) and C) is carried out in an aqueous medium, for example by adding A) in solid form or as an aqueous concentrate gradually to an aqueous solution of C), preferably containing 30—50% C) and 50—70% water by weight. The aqueous medium preferably has a pH between 4 and 6.

It is strongly preferred that the catalyst D) be present during the reaction of A) and C) to form the precondensate B). Suitably it is dissolved in the aqueous solution of C) before addition of A). However, if A) and C) can react together adequately in the absence of D), then the catalyst D) may be added to the precondensate subsequently.

A) and C) are reacted together, preferably with constant stirring, at room temperature or at temperatures of up to 80°C, preferably 60—80°C more preferably 70—75°C. The condensation reaction should be stopped before the reaction product becomes water-insoluble or forms a gel; suitable reaction times are of the order of 30 minutes to 3 hours. The final product preferably has a viscosity at room temperature of 50—200 centipoise, more preferably 60—150 c.p. These viscosities apply to the reaction products as they are obtained i.e. including water in amount 30—60% (by weight).

The relative amounts of components A), C) and D), if present, fall within the limits 5—40 parts by weight A), 25—110 parts by weight C), 1—30 parts by weight D), calculated on the basis of the active component present. Expressed as a weight ratio, the ratio of A:C:D is 1:0.625—22:0.025—6. Preferred ranges are 10—20 parts by weight A), 35—75 parts by weight C) and 5—15 parts by weight D), or 1:1.75—7.5:0.25—1.5; more preferably 1:2—3:0.5—1.

Suitable catalysts D) are of the type used for the crosslinking of N-methylol compounds C) on cellulose, and examples are given in British Patent Application 2 070 006A. Preferred catalysts are the nitrates, sulphates, chlorides and dihydrogen orthophosphates of aluminium, magnesium or zinc, more preferably or magnesium, particularly magnesium chloride, optionally together with an alkali metal sulphate, particularly sodium sulphate.

According to the process of the invention, a substrate comprising a mixture of natural or synthetic polyamide fibres and hydroxy group-containing fibres is first dyed or brightened sequentially or simultaneously with dyestuffs or

optical brighteners suitable for each fibre component, then is after-treated with precondensate B) in the presence of catalyst D) or with component A) alone.

The polyamide component may be wool or may be a synthetic polyamide for example nylon 6 or nylon 66. The hydroxy group-containing component is preferably a cellulosic fibre, particularly cotton. Preferred substrates have a polyamide:cellulose ratio between 20:80 and 80:20, more preferably 50:50. The polyamide component is dyed using a suitable anionic dyestuff; the cellulose component with a direct or reactive dye. The substrate may be dyed or printed by any methods conventionally used for these dyestuffs; for example dyeing may be carried out by exhaust dyeing from a dyebath, or by padding followed by a thermofixation or cold dwell fixation, or, in the case of reactive dyes, by alkaline fixation.

The process according to the invention is carried out upon a substrate on which the dyeing or printing process, including any necessary fixation step, has been completed. The substrate may be dry or may still be damp, provided that it is not so wet that it is incapable of further pick-up.

When component A) is used alone, this is preferably applied by an exhaust process from a short or long bath. In a long bath (liquor to goods ratio above 10:1), the quantity of component A) (measured as dry active substance) in the bath is preferably from 1 to 10 g/l, more preferably 2—5 g/l. In short bath processes quantities of 20—100 g/l may be necessary. Preferred application conditions are a temperature of 30—70°C, pH 4—5 for a time of 10—60 minutes.

When precondensate B) is used together with catalyst D), the aftertreatment agent may be applied to the surface in aqueous solution by dipping, spraying, foam application, padding or other conventional application techniques. The preferred application method is by padding at room temperature.

The quantities in which the product according to the invention is applied to the substrate depend largely upon the depth of the dyeing which is to be fixed. For dyeings of 1/1 standard depth the quantities used are 30—200 g/l of the padding liquor when applied at a pick-up of 70—100% of the dry weight of the goods. Preferably the quantity is 70—130 g/l calculated on the basis of the total dry weight of the substrate.

After the application of the padding liquid, the substrate is subjected to a heat curing step such as is conventional for resin treatments based on compounds of type B). The substrate may for example be dried at 70—120°C and finally cross-linked at a temperature of 130—180°C for 30 seconds to 8 minutes, or alternatively simultaneously dried and cross-linked by heat treatment at 120—200°C, preferably 140—180°C for 5 seconds to 8 minutes depending on the temperature. A preferred process involves heating the padded substrate to 150—170°C for 60 to 90 seconds.

Particularly suitable direct and reactive dyestuffs for use on the cellulosic component of the substrate are described in British Patent Application 2 070 006A, and in British Patent

5 Application 2 093 076A.

Preferred anionic dyestuffs for use on the polyamide component of the substrate, particularly for synthetic polyamide, are anionic mono- or polysulphonated dyestuffs of molecular

10 weight from 400—1000, optionally in metal complex form. More preferred dyestuffs have at least two sulphonic acid groups and a molecular weight of 600—1000, optionally in metal complex form, particularly metal complex forms

15 having a molecular weight of 800—1000.

A preferred group of dyestuffs are C.I. Acid Dyes which exhaust on to nylon 6 to the extent of at least 50% from an aqueous bath containing twice the amount required to give a 1/1 standard

20 depth dyeing, at a goods-to-liquor ratio of 1:30 after 60 minutes at pH 3—11 and a temperature of 30—98°C.

Suitable acid dyes are disclosed in the following patent literature: German Patents

25 1 644 356, 2 013 783, 2 153 548, German published applications (DOS) 2 202 419, 2 400 654, 2 631 830, 2 729 915, 3 034 576; French Patents 7 506 109 and 7 624 658.

The polyamide component may also be dyed with reactive dyestuffs which are conventional for use on polyamide fibres.

Although these aftertreatment agents are known for the fixation of dyeings on cellulose, it is surprising that they also give improved fastness properties for dyeings on the polyamide component of the mixed textile substrate, although both the substrate and the dyes employed are chemically quite different. Improved fastness properties include wet fastness, e.g. wash

35 fastness, sweat fastness, and water fastness, as well as, in some cases, improved light fastness.

The following Examples, in which all parts and percentages are by weight and all temperatures in degrees centigrade, illustrate the invention.

45 *Preparation of after-treatment agents* (according to British Patent Application 2 070 006A)

A i) 103 Parts diethylene triamine and 84 parts dicyandiamide (DCDA) are slowly heated to 100—110°C. After ammonia ceases to be evolved, the temperature rises to 160°C, and the mixture is reacted for 6 hours at this temperature. The reaction mass is cooled, neutralised with dilute sulphuric acid and spray dried.

ii) 25 Parts of the product A i) is mixed with 15 parts  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 100 parts of a 50% aqueous solution of dimethyloldihydroxyethylene-urea, and the mixture reacted for 1 hour at 70°, to give a cloudy water-miscible liquid.

B i) Preparation A i) is repeated using 175.5 parts 3-(2-aminoethyl)-aminopropylamine in place of diethylene triamine, reacting at a temperature of 120°C.

ii) Preparation A ii) is repeated using 25 parts of the product B i).

65 C i) Preparation A i) is repeated using 120 parts

ethylene diamine in place of diethylene triamine.

ii) Preparation of A ii) is repeated using 25 parts of the product of C i).

#### EXAMPLE 1

70 A mixed textile fabric comprising 20 parts nylon 6 and 80 parts cotton is dyed in conventional manner using C.I. Acid Red 128 for the polyamide component and the dyestuff of formula VII of British Patent Application 2 070 006A for the

75 cotton component, both in 1/1 standard depth.

The dyed fabric is then padded at 80% pick up with a padding liquor containing 12% of the product A ii) and 0.5% 80% acetic acid, and the fabric is dried then heat-cured for 40 seconds with hot air at 180°. The after treated dyeing has improved wet-, wash- and chlorinated water fastness.

#### EXAMPLES 2—4

85 The procedure of Example 1 is repeated, using the dyestuffs C.I. Acid Blue 113, C.I. Acid Red 399 or C.I. Acid Blue 310 respectively for the polyamide component in place of C.I. Acid Red 128. Similar good results, including improved light fastness, are obtained.

#### 90 EXAMPLE 5

Example 1 is repeated, using the same padding liquor with the addition of 4% of a cationic softener and 0.1% of a non-ionic surfactant. Equally good results are obtained.

#### 95 EXAMPLE 6

A mixed textile substrate consisting of 50 parts nylon 66 and 50 parts cotton is dyed in conventional manner with C.I. Acid Blue 296, C.I. Acid Blue 225 and C.I. Direct Blue 251, and aftertreated as described in Example 1. The dyeings on both the nylon and the cotton component show improved wet- and wash-fastness properties.

#### EXAMPLES 7, 8

105 Example 6 is repeated using the products B ii) and C ii) respectively in place of product A ii). Equally good results are obtained.

#### EXAMPLE 9

110 A mixed textile substrate consisting of 50 parts nylon 66 and 50 parts cotton is dyed in conventional manner with the dyestuffs C.I. Acid Red 119 and the dyestuff of formula VIII of British Patent Application 2 070 006A.

The dyed fabric is after-treated by an exhaust process at a goods-to-liquor ratio of 1:20 at 50° for 20 minutes in a bath containing 0.1% of product A i) and 0.025% glacial acetic acid (based on the weight of the bath), to give a pH value of 4.5.

120 The after-treatment fabric is rinsed and dried, and shows improved sweat- and water-fastness.

#### EXAMPLE 10

A mixed textile substrate as in Example 9 is

printed with a conventional printing paste containing the dyestuffs of Example 1, and is aftertreated as described in Example 1. Good results are obtained.

#### 5 EXAMPLE 11

A mixed textile substrate consisting of 50 parts wool and 50 parts cotton is dyed in a conventional single bath process at a goods-to-liquor ratio of 1:30 in a dyebath containing 0.025% C.I. Direct Green 69, 0.02% C.I. Acid Green 106 and 0.006% C.I. Acid Blue 225.

The dyed and rinsed substrate is after-treated at the same goods-to-liquor ratio in a bath containing 0.1% of the product A i), 0.05% glacial acetic acid (to pH 5) and 0.05% NaCl. Aftertreatment is carried out at 30—60° for 20—30 minutes, and the substrate is finally rinsed and dried. The aftertreated dyeing has improved wet fastness properties.

#### 20 EXAMPLE 12

A mixed textile substrate of 30 parts wool and 70 parts cotton is dyed as in Example 11 in a dyebath containing 0.01% C.I. Direct Yellow 162, 0.08% C.I. Direct Red 83, 0.02% C.I. Acid Red 399 and 0.01% C.I. Acid Violet 128. The dyed and rinsed substrate is padded as in Example 1 with a padding liquor containing 8% product A ii) and 0.2% acetic acid (to pH 4.5—5), and finally dried and heat-cured at 140—160° for 3—6 minutes.

30 The treated substrate shows improved wet fastness properties.

#### EXAMPLE 13

Example 12 is repeated, using in the dyebath 0.008% C.I. Direct Yellow 162, 0.03% C.I. Direct Brown 240, 0.03% C.I. Direct Blue 251 and 0.05% C.I. Acid Black 222, with the same aftertreatment agent. Equally good wet fastness properties are obtained.

#### EXAMPLE 14

40 A mixed textile substrate consisting of 50 parts nylon 6 and 50 parts cotton is treated in a first step at 1:20 goods:liquor ratio with a mildly alkaline bath containing 0.07% C.I. Reactive Orange 64 and 0.05% C.I. Reactive Red 159 to dye the cotton. In a second step the polyamide component is dyed at the same goods:liquor ratio with a neutral to weakly acid bath containing 0.03% C.I. Reactive Orange 64, and 0.02% C.I. Reactive Red 159,

50 and the dyeings are fixed in conventional manner.

The dyed substrate is after-treated as described in Example 9 with the product A i), giving improved wet fastness properties.

#### EXAMPLE 15

55 The dyeing of Example 14 is aftertreated as described in Example 1 using product A ii). Equally good results are obtained.

#### CLAIMS

1. A process for improving the fastness

60 properties of dyestuffs or optical brighteners on a substrate comprising a mixture of natural or synthetic polyamide fibres and hydroxy group-containing fibres, by applying to the dyed, printed or brightened substrate either

65 A) a polybasic compound which is the product of reacting a mono- or polyfunctional primary or secondary amine with cyanamide, dicyandiamide (DCDA), guanidine or biguanidine; whereby up to 50 mole % of the cyanamide, DCDA, guanidine or biguanidine may be replaced with the dicarboxylic acid or a mono- or di-ester thereof, said product A) containing reactive hydrogen atoms bound to nitrogen, or

75 B) a precondensate formed by reacting A) above with

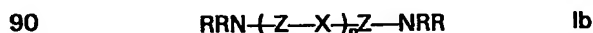
C) an N-methylol derivative of a urea, melamine, guanamine, triazinone, urone, carbamate or acid amide applied to the substrate together with

80 D) a catalyst for the crosslinking of N-methylol compounds of the type C) above provided that, when precondensate B) and catalyst D) are applied, then a final heat-curing step is carried out.

85 2. A process as claimed in Claim 1 in which component A) is the reaction product of a monofunctional amine of formula Ia



or a polyfunctional amine of formula Ib



in which each R independently is hydrogen or a C<sub>1-10</sub> alkyl group unsubstituted or monosubstituted with hydroxy, C<sub>1-4</sub> alkoxy or cyano, provided that in formula Ia, at least one R is other than hydrogen;

95 n is a number from 0 to 100; Z, or each Z independently when n > 0, is C<sub>1-4</sub> alkylene or hydroxyalkylene; and

100 X, or each X independently when n > 1, is —O—, —S— or —NR— where R is as defined above, provided that the amine of formula Ib contains at least one reactive —NH— or —NH<sub>2</sub> group, with cyanamide, dicyandiamide (DCDA) or guanidine.

105 3. A process as claimed in Claim 2 in which component A) is the reaction product of a polyfunctional amine of formula Ib in which R is hydrogen or C<sub>1-4</sub> alkyl or hydroxyalkyl, n is an integer from 1—6 and X is —NR—, with cyanamide, DCDA or guanidine.

110 4. A process as claimed in Claim 3 in which component A) is the reaction product of ethylene diamine, triethylene tetramine or 3-(2-aminoethyl)-aminopropylamine with DCDA.

115 5. A process as claimed in any one of Claims 1—4 in which component A) is applied alone by an exhaust process.

120 6. A process as claimed in Claim 5 in which the application is carried out at 30—70°C, pH 4—5,

for 10—60 minutes.

7. A process as claimed in Claim 5 or Claim 6 in which the application is carried out from a long bath containing from 1 to 10 g/l of component A).

5 8. A process as claimed in any one of Claims 1—4 in which component C) is N,N'-dimethylol-4,5-dihydroxy- or 4,5-dimethoxyethyleneurea, N,N'-dimethyl-4-methoxy-5,5-dimethylpropyleneurea and N,N'-dimethylol carbamate or a methyl or ethyl ether of any of these.

10 9. A process as claimed in any one of Claims 1—4 and 8 in which catalyst D) is selected from the nitrates, sulphates, chlorides and dihydrogen orthophosphates of aluminium, magnesium and zinc.

15 10. A process as claimed in Claim 9 in which component C) is N,N'-dimethylol-4,5-dihydroxyethyleneurea and catalyst D is magnesium chloride.

20 11. A process as claimed in any one of Claims 1—4, and 8—10 in which precondensate B) is prepared by reacting components A) and C) in an aqueous medium in the presence of catalyst D).

25 12. A process as claimed in any one of Claims 1—4 and 8—11 in which the weight ratio of A:C:D is 1:0.625—22:0.025:6.

30 13. A process as claimed in any one of claims 1—4 and 8—12 in which precondensate B) is applied to the substrate by padding at room temperature.

14. A process as claimed in Claim 13 in which the padding liquor contains 30—200 g/l of

precondensate B), and is applied at a pick-up of 70—100% of the dry weight of the goods.

35 15. A process as claimed in any one of Claims 1—4 and 8—14 in which the heat-curing step is carried out by heating to 150—170°C for 60 to 90 seconds.

40 16. A process as claimed in any one of the preceding claims in which the substrate is a mixture of cotton with wool, nylon 6 or nylon 66, in a ratio of from 20:80 to 80:20 by weight.

45 17. A process as claimed in Claim 16 in which the cotton is dyed or printed with a direct or reactive dye and the polyamide is dyed or printed with an anionic dye.

50 18. A process as claimed in Claim 17, in which the polyamide is dyed with an anionic dyestuff having at least two sulphonic acid groups and a molecular weight of 600—1000, optionally in metal complex form.

55 19. A process as claimed in Claim 17 in which the polyamide is dyed with an anionic dyestuff which is selected from C.I. acid dyes which exhaust on to nylon 6 to the extent of at least 50% from an aqueous bath containing twice the amount required to give a 1/1 standard depth dyeing, at a goods-to-liquor ratio of 1:30 after 60 minutes at pH 3—11 and a temperature of 30—98°C.

60 20. A process for improving the fastness properties of dyestuffs on a substrate comprising a mixture of natural or synthetic polyamide fibres and cotton, as described in any one of the Examples.